

Claim 13 has been amended to recite a process according to claim 12 wherein at least a portion of the separated peracid-containing phase is treated to remove at least a portion of the sulfur-containing and nitrogen-containing organic compounds contained therein, and thereafter recycled to the reaction mixture. Support for this amendment is found in the Specification, for example, at page 27, lines 20 to 24.

In view of the amendments submitted herein, it is the position of Applicants that the instant Application is in condition for allowance.

#### Prior Rejections

Applicants and their undersigned Attorney note with appreciation that the rejections under 35 U.S.C. § 112, second paragraph, and under 35 U.S.C. § 102(b) and (e) as described in paper no. 2 have been withdrawn by Examiner Griffin in response to the amendment filed on October 8, 2002.

#### Claim Rejections - 35 U.S.C. § 103

In the outstanding Office Action, Claims 1 to 3 and 5 to 10 were rejected under 35 U.S.C. § 103(a), as being unpatentable over U.S. Patent No. 1,972,102 in the name of William M. Malisoff (Malisoff), in view of U.S. Patent No 6,217,748 in the name of Shigeto Hatanaka, Osamu Sadakane, and Hideshi Iki and assigned to Nippon Mitsubishi Oil Corp. (JP), (Hatanaka et al.). Applicants respectfully traverse these rejections.

The Malisoff reference of record describes a treatment for removal of sulfur from hydrocarbon oil by washing the oil with a treating solution containing acetic acid and hydrogen peroxide in water.

The Hatanaka et al. reference of record describes a four-step hydrodesulfurization (HDS) of a sulfur-containing petroleum hydrocarbon diesel gas oil. The gas oil is catalytically hydrodesulfurized at 300° C. to about 500 ppm sulfur in a first HDS step. Step two is distillation at a cut point temperature in a range of 320 to 340° C. Step three is a second HDS at 320 to 380° C., but of only the heavy fraction of the distillation. The twice hydrodesulfurized heavy fraction (90 ppm sulfur) is mixed with the light fraction of the distillation (10 ppm sulfur) to a sulfur content of up to 0.01% (50 ppm sulfur, Hatanaka et al. Example 3).

Obvious disadvantages of the Hatanaka et al. process include the costs of the additional hydrogen and energy required for both the distillation and further hydrodesulfurization steps. While Hatanaka et al. state the hydrogen sulfides from the two HDS steps may be removed from the off-gas by an amine absorption arrangement, carbon oxides are also by-products of the HDS steps. Generation of the additional hydrogen also produces more carbon dioxide. These are especially critical at a time when most industries are striving to limit the amount of emitted "green house" gas such as carbon dioxide.

Less obvious disadvantages of the second HDS in the Hatanaka et al. process include a loss of non-sulfur multi-ring aromatic hydrocarbons to saturated non-aromatic ring compounds. This has negative fuel property/quality consequences such as affecting the pour point, reducing the lubricity, and reducing the fuel value (Btu/volume) of diesel fuel. A diesel fuel rich in aromatics have a higher Btu/volume and give more miles per gallon.

The oxidation step in Applicants' novel process is very specific in the targeting of sulfur hetroaromatic compounds. Oxidation of these offending sulfur hetroaromatics is selective and other aromatic hydrocarbons not containing sulfur or nitrogen are unaffected by the process.

Contrary to the position of Examiner, substituting the oxidation treatment of Malisoff for the second HDS of Hatanaka et al. does not produce an equivalent result.

By contrast Applicants' novel process includes a catalyzed, 5 hydrogen peroxide, promoted oxidative desulfurization of a sulfur-rich, mono-aromatic-lean fraction without further production of carbon dioxide or hydrogen sulfides. An additional advantage of Applicants' novel oxidative desulfurization process is that oxidation is selective to sulfur and nitrogen containing heteroaromatic 10 compounds, i.e. does not saturate the non-sulfur, non-nitrogen multi-ring aromatic hydrocarbons.

It is the position of Applicants that instant Claim 1 and dependent Claims 2, 3, and 5 to 10, (as well as Claim 4) meet all requirements under 35 U.S.C. § 103(a).

15       Claim 4 was rejected under 35 U.S.C. § 103(a), as being unpatentable over U.S. Patent No. 1,972,102 (Malisoff), in view of U.S. Patent No 6,217,748 (Hatanaka et al.) as applied to Claim 1, and further in view of U.S. Patent No 6,402,940 in the name of Alkis S. Rappas (Rappas). Applicants respectfully traverse these rejections.

20       Claims 1, 2, and 4 to 11 were rejected under 35 U.S.C. § 103(a), as being unpatentable over U.S. Patent No 6,402,940 (Rappas) in view of U.S. Patent No 6,217,748 (Hatanaka et al.). Applicants respectfully traverse these rejections.

25       Claims 12 to 20 were rejected under 35 U.S.C. § 103(a), as being unpatentable over U.S. Patent No 6,402,940 (Rappas) in view of U.S. Patent No 6,217,748 (Hatanaka et al.), and further in view of U.S. Patent No. 3,163,593 in the name of Alfred Bentley Webster, Norman James Herbert, and Richard Rigby (Webster et. al.). Applicants respectfully traverse these rejections.

The Rappas reference of record describes a process for removing low amounts of organic sulfur from hydrocarbon fuels using an oxidizing/extracting solution of formic acid, a small amount of hydrogen peroxide, and no more than about 25 wt % water.

A declaration under 37 CFR § 1.131 of prior invention by Applicants, identified as Paper No. 8, is hereby presented to further the prosecution of subject Application. In particular, the declaration is a showing of facts which establish that reduction to practice of Applicants' invention, as described and claimed in subject application, was completed in the United States of America prior to September 1, 2000, the filing date of the application from which U.S. Patent No. 6,402,940 (Rappas) matured.

Applicants respectfully request Primary Examiner Griffin to withdraw all rejections under 35 U.S.C. § 103 (a) which rely upon the Rappas reference of record in any combination with the Hatanaka et al., Malisoff, and/or Webster et al. references of record.

Base on the amendments submitted herein, and previously, and Paper No. 8 declaration under 37 CFR § 1.131, Applicants urge that Claims 1 to 20 inclusive, all claims now presented, are in condition for allowance. Applicant respectfully requests Primary Examiner Griffin to pass subject application for allowance.

Do not hesitate to contact Frederick S. Jerome whose telephone number is (630) 832-7974 (FAX (630) 832-7976) if additional assistance is needed regarding this paper or earlier papers for Applicants.

09/779,285 filed 2/8/01

Applicants and their undersigned Attorney appreciate Examiner's attention and further consideration of this matter.

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Respectfully submitted,

Frederick S. Jerome

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Version of Amended Claims with Markings  
to Show Changes Made

1. (Twice amended) A process for the production of  
5 refinery transportation fuel or blending components for refinery  
transportation fuel, which process comprises:

providing an oxidation feedstock comprising a mixture of  
hydrocarbons, sulfur-containing and nitrogen-containing organic  
compounds, which mixture has a gravity ranging from about 10° API  
10 to about 100° API and is a product of a hydrotreating process for  
petroleum distillate;

15 contacting the oxidation feedstock with an immiscible phase  
comprising at least one organic peracid or precursors of organic  
peracid, in a liquid reaction mixture maintained substantially free of  
catalytic active metals and/or active metal-containing compounds and  
under conditions suitable for oxidation of one or more of the sulfur-  
containing and/or nitrogen-containing organic compounds; and

20 separating at least a portion of the immiscible peracid-containing  
phase from the reaction mixture;

treating the immiscible peracid-containing phase separated from  
the reaction mixture to remove at least a portion of the sulfur-  
containing and nitrogen-containing organic compounds contained  
therein ; and

25 recovering a product comprising a mixture of organic compounds  
containing less sulfur and/or less nitrogen than the oxidation  
feedstock from the reaction mixture.

30 4. (Once amended) The process according to claim 1  
[wherein] further comprising recycling at least a portion of the  
[separated] treated peracid-containing phase [is recycled] to the  
reaction mixture.

13. (Once amended) The process according to claim 12  
wherein at least a portion of the separated peracid-containing phase is  
treated to remove at least a portion of the sulfur-containing and  
nitrogen-containing organic compounds contained therein, and  
5 thereafter recycled to the reaction mixture.

*HS*

PATENT APPLICATION



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

RECEIVED

In re the Application of:

) Paper No. 8 FEB 14 2003

APPLICANTS: WILLIAM A. GONG,  
MONICA C. REGALBUTO, &  
GEORGE A. HUFF JR.

)  
TC 1700

)  
04249

PATENT TRADEMARK OFFICE

SERIAL NO: 09/779,285

) Group Art Unit:

) 1764

FILED: February 8, 2001

) Examiner:

) Walter D. Griffin

FOR: PREPARATION OF COMPONENTS FOR  
REFINERY BLENDING OF  
TRANSPORTATION FUELS

) Attorney Docket

) No.: 37,248

)

**DECLARATION UNDER 37 CFR § 1.131**

Assistant Commissioner for Patents  
Washington, DC 20231

ANY ADDITIONAL FEES REQUIRED  
CHARGE TO DEPOSIT ACCOUNT  
NO. 01-0528

**CERTIFICATE OF MAILING**

I hereby certify that this correspondence is being deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to:  
Commissioner of Patents and Trademarks, Washington, D.C. 20231

on February 5 2003. By Carol M. Neth  
(Date) (Signature)

CAROL M. NETH

(Typed or Printed Name of Person Signing Certificate)

Examiner Griffin:

William H. Gong, Monica R Regalbuto and Gerore A. Huff, Jr. hereby solemnly declare that:

5        1. They are the inventors who, on February 8, 2001, filed the above-identified application Serial No. 09/779,285.

10      2. They completed the invention, which is set forth in the above-identified application Serial No. 09/779,285, in the United States of America prior to September 1, 2000, the filing date of the application from which U.S. Patent No. 6,402,940 (Rappas) matured.

3. Prior to September 1, 2000, our invention as described and claimed in the subject application was completed in the United States, as evidenced by the following Exhibits:

15      a     Laboratory Notebook 20164, pages 37 and 38, identified as EXHIBIT A, illustrates the key points of my oxidation and simultaneous extraction of a high boiling fraction of diesel fuel.

20      b     Laboratory Notebook 20453, pages 44 to 47, identified as EXHIBIT B, illustrates the key points of my liquid-liquid extraction of an oxidized high boiling fraction of diesel fuel to remove residual sulfur.

These Exhibits memorialize and record experiments carried out in Naperville, Illinois, which serve to reduct the aforesaid invention to practice.

25      4. Under the supervision of Dr. William H. Gong, who is one of the undersigned declarants, Mrs. Christine Peaches, a BP Amoco Research Technician, conducted an oxidation-simultaneous extraction experiment described in an Amoco Research Notebook 20164, pages 37 to 38. In this experiment, Mrs. Peaches created a biphasic mixture comprising of 100 g of a high boiling fraction of diesel fuel (a.k.a. LS-98-25-A600 but also labeled as "LS-98-150-

A600" which fraction boiled above 600° F (316° C) and contained 580 ppmw sulfur), 34 milliliter of 30 percent by weight hydrogen peroxide, 50 milliliter of glacial acetic acid (HOAc), and 50 milliliter of distilled and deionized water (D&D water). This mixture was  
5 created in a 3-neck, round bottom flask equipped with an overhead agitator, a water-cooled reflux condenser, a nitrogen inlet and outlet, and a heating mantel.

5. The mixture was heated to boiling (approximately 210°  
F) with an agitation rate fixed at 200 rpm, and was sustained at  
10 this temperature for 120 minutes (2 hours). After this heating period had elapsed, the heating mantel was switched off and the agitation was temporarily ceased to permit a disengagement of the diesel layer from the aqueous acetic acid layer. The top layer, the oxidized and extracted diesel immiscible layer, was sampled for  
15 sulfur analysis. After the sampling, the agitation was resumed until the mixture was cooled. Approximately 0.1 grams of manganese dioxide was added to the mixture to decompose any unused peroxide in the aqueous acetic acid layer. The entire reactor content was transferred to a storage container. The  
20 bottom, aqueous acetic acid layer, was sampled for sulfur analysis.

6. The oxidized and extracted diesel layer was determined to contain 355 ppmw sulfur (LIMS sample number 152051) while the bottom, aqueous acetic acid layer was determined to contain 41 ppmw sulfur (LIMS sample number 152084). These results  
25 demonstrate a desulfurization of the diesel layer due to oxidation and simultaneous extraction of sulfur into the aqueous acetic acid layer.

7. As EXHIBIT B, illustrates, Mr. Donald J. Maciejewski, a BP Amoco Research Technician, conducted a liquid-liquid extraction of a hydrogen peroxide, acetic acid-based oxidation of a diesel fuel which boiled above 600 OF (316° C) and contained 580 ppmw sulfur and 147 ppmw nitrogen. The experiment required the preparation of a large volume (approximately one liter) of an  
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"oxidized and simultaneously extracted oxidized diesel fuel" (from this point on known as the "oxidized diesel") to test the concept of the liquid-liquid extraction. This oxidized diesel fuel was prepared according to the instructions documented in Research Notebook number 20453, pages 44 to 46. The oxidized diesel fuel product obtained from this procedure was significantly desulfurized and denitrogenated as the product fuel contained 143 ppmw sulfur and 4 ppmw nitrogen (LIMS sample manager number 155378). The aqueous acetic acid layer separated after the oxidation-extraction procedure was found to have a sulfur concentration of 252 ppmw or 0.0252 percent by weight (LIMS sample manager number 155377), thus demonstrating that during the oxidation, an effective extraction of the oxidized diesel impurities occurred. After the oxidized diesel fuel was dehydrated by treatment with molecular sieves, the oxidized product is then identified as the "dried" diesel product.

8. The "dried" diesel product was then submitted for solubility testing in four different liquid-liquid solvent candidates. This work by Mr. Donald J. Maciejewski, is described in Research Notebook number 20453 on page 47. The test was to result in the selection of a feasible solvent which must be immiscible with the diesel product and that after mixing, the diesel product must separate quickly from the solvent layer.

9. Mr. Maciejewski found that methanol met the two criteria and his observations are recorded in Amoco Research Notebook number 20453 on page 47. Subsequent work by Mr. Maciejewski demonstrated that after one extraction with methanol, the "dried" oxidized, methanol extracted product contain only 35 ppmw sulfur and 3 ppmw nitrogen (LIMS sample manager number 157666). These results demonstrate the effectiveness of their procedure in reducing the sulfur and nitrogen content of LS-98-150-A600, which originally contained 580 ppmw sulfur and 147 ppmw nitrogen.

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10. Copies of the above referenced Laboratory Notebook pages are attached as Exhibits. The Exhibits are a true copy, except that the dates thereof and unrelated subject matter have been blanked-out, but all the dates are prior to September 1, 2000.

5        11. The undersigned declare further that at all statements made herein of their own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable  
10 by fine or imprisonment, or both, under 18 U.S.C. 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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William H. Gong  
WILLIAM H. GONG

Date February 3, 2003

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Monica C. Regalbuto  
MONICA C. REGALBUTO

Date Jan 30, 2003

George A. Huff, Jr.  
GEORGE A. HUFF, JR.

Date Feb 3, 2003



20164

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Project No. PL0001Z-4.01 Date of Work \_\_\_\_\_

Continued From Page \_\_\_\_\_

Title or Purpose: Hydrogen Peroxide Oxidation of High Boiling Fraction**KEYWORDS:** Diesel Fuel (HS-98-25-A600)

Run # 20164-037-1

Flash Charged:

LS-98-150-A600	—	100g.
30% H <sub>2</sub> O <sub>2</sub> (ML)	—	340
GLACIAL H <sub>2</sub> O <sub>2</sub> (ML)	—	50
D&D WATER (ML)	—	50

Into a 250mL, three-neck round bottom flask equipped with a reflux condenser, mechanical agitator, a Nitrogen inlet and outlet set at 1.0 are charged the above, and heated at 100°C for 2hrs. Stirred also at 20 rpm. After the end of the 2hrs are up, from the top layer is sampled with 15mL and stored into a plastic 4-dram vial with the cap loosely fixed in case there are residual peroxides decomposing. Sample are transferred to T.J. Barnes for submit to Sample Manager. The sample stirred and cooled to room temperature. Once at room temperature used 0.1g of manganese dioxide is added to decompose of the excess hydrogen peroxide and then stirred for 10 minttles more. Entire sample is then poured into a bottle with a vented cap.

(OVER)

Work By Chris PeachesContinued on Page 38Recorded By Chris Peaches

38

Project No. Rhonor 4:01 Date of Work \_\_\_\_\_ Continued From Page \_\_\_\_\_

Title or Purpose: \_\_\_\_\_

**KEYWORDS:****Clean up Equipment:**

The (Flask, Agitator, Thermometer, Condenser) Are then rinsed with acetone and disposed according to Safety Procedure. After the organic residue has been removed, the equipment is then rinsed with distilled water and allowed to air dry.

Sample # 20164-039-1  
WEIGHT For 15ML Sample  
11.93g. 12.447g.  
FINAL Large Bottle Sample WT. 210.024g.

Work By Chris Peaches \_\_\_\_\_ Continued on Page \_\_\_\_\_  
Reviewed By Chris Peaches \_\_\_\_\_ Date 2/8/01

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Project No. \_\_\_\_\_ Date of Work \_\_\_\_\_ Continued From Page \_\_\_\_\_

Title or Purpose: Oxidative Desulfurization of LS-98-150-A600 (600 to FBP)**KEYWORDS:****Oxidative Desulfurization of LS-98-150-A600 (600 to FBP)**

**Note:** This procedure is for a one-liter scale and can be scaled proportionally to equipment of different sizes

**Procedure**

Into a three (3) or four (4) liter, three neck, round bottom flask equipped with a water-jacketed reflux condenser, a mechanical stirrer, a nitrogen inlet and outlet, a temperature controller (eurotherm and thermocouple) and a heating mantel, are charged with.

- <sup>>600 T</sup>  
one (1) kg of LS-98-150-A600
- one (1) liter of glacial acetic acid
- 170 mL of 30% hydrogen peroxide ( $H_2O_2$ ).

A slight flow of nitrogen is initiated and this gas then slowly sweeps over the surface of the reactor content. The agitator is started to provide efficient mixing and the contents are heated. Once the temperature reaches 200 °F, the contents are heated for 120 minutes at this temperature.

After the reaction time has elapsed, the contents are continuing to be stirred with the heating mantel turned off and removed. At approximately 170 °F, the agitator is stopped momentarily while approximately 1 g of manganese dioxide ( $MnO_2$ ) is added through one of the necks of the round bottom flask to the biphasic mixture to decompose any unreacted hydrogen peroxide. Mixing of the contents with the agitator is then resumed until the temperature of the mixture has cooled to approximately 120 °F. The agitation is ceased to allow both organic (top) and aqueous (bottom) layers to separate (should occur immediately).

The bottom layer is removed and isolated either by vacuum with the aid of a dip tube or some other equivalent procedure. Note: It isn't necessary to remove every last bit of the bottom layer; leaving behind a bit of this is not detrimental to the following procedure. The bottom layer is to be saved for further analysis. It is necessary that the aqueous acetic acid layer is stored in a lightly capped bottom to permit the evolution of oxygen

Into the reactor is charged with 500 mL of saturated aqueous sodium bicarbonate to neutralize the organic layer (CAUTION: WHEN ADDING THIS SOLUTION, BE CERTAIN THAT THE AGITATOR IS STIRRING SLOWLY AND ADD THIS SOLUTION SLOWLY AS GAS ( $CO_2$ ) EVOLUTION WILL OCCUR INITIALLY). After the bicarbonate solution has been added, allow the mixture to stir rapidly for five to ten minutes to neutralize any remaining acetic acid. Remove the bottom, aqueous layer, and isolate the top layer. Dry the organic material over anhydrous 3 angstrom

Work By \_\_\_\_\_

*AJ Mazzola*

Continued on Page

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Recorded By \_\_\_\_\_

Read and Understood By \_\_\_\_\_

Serial No. 09/779,285

Declaration under Rule 1.131

EXHIBIT B

20453

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Project No. \_\_\_\_\_ Date of Work \_\_\_\_\_ Continued From Page 44Title or Purpose: OXIDATIVE DESULFURIZATION OF LS-98-150 A600 1000 TO FB01**KEYWORDS:**

molecular sieve. After the material has been dehydrated by the molecular sieve, remove the sieve by filtration and isolate the filtrate.

Analytical Chemistry

1. Submit a sample of the first aqueous acetic acid layer for OELECOSHT.
2. Submit a sample of the organic layer for the following: OELECOSHT, OENPPMWOIL, CCTAN

Sodium Bicarbonate Aqueous Saturated Solution  
90.01 g

LS - 98-150 FRACTION 5 POT  
 1160 ml = 1000.9 g  
 1L GLACIAL ACETIC ACID 170 ml 30% HYDROGEN PEROXIDE  
 9:50 REACTOR = 204°/ (OFF AT 11:50 AM)  
 12:15 PROCEDE AT 175°/ ADD 500 ml 1.0049g MANGANESE(IV) OXIDE  
 TUMBLE MIXER ON AND LET SOLUTION COOL TO 120°/ 99.99.  
 14:40 REACTOR AT 115°/ USED DIP TUBE TO REMOVE BOTTOM  
 LAYER 20453-45-1 (AQUEOUS ACETIC ACID B.T.3 LAYER)

ADDED 500 ml OF SATURATED SODIUM BICARBONATE SOLUTION Slowly  
 WHILE MIXTURE WAS TUMBLING AT 60 RPM.  
 AFTER ALL THE SODIUM BICARBONATE WAS ADDED THE STIRRER  
 WAS INCREASED TO 200 RPM FOR 10 MINUTES.  
 MIXTURE WAS Poured INTO A 2000 ml SEPARATORY FUNNEL  
 TO ALLOW THE LAYERS TO SEPARATE.

20453-45-2 AQUEOUS SODIUM BICARBONATE  
 20453-45-3 ORGANIC LAYER

Work By \_\_\_\_\_ Continued on Page 46

Recorded By DJ Maileyah Date \_\_\_\_\_

Read and Understood By \_\_\_\_\_

Date \_\_\_\_\_

Serial No. 09/779,285

Declaration under Rule 1.131

EXHIBIT B

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Project No. \_\_\_\_\_ Date of Work \_\_\_\_\_

Continued From Page 45

Title or Purpose: \_\_\_\_\_

**KEYWORDS:**

Dries the Organic Layer by adding 3A Molecular Sieve to  
the bottle and let sit overnight.

Filters the Organic Layer through Millipore LC 10.0µm Filter  
20453-046-1

<u>1712.9</u>	<u>1684.3</u>
<u>840.3</u> g	<u>840.3</u>
<u>872.6</u> g	<u>844.0</u> g

ANALYTICAL

Acne Acn 20453-045-1

OELCOSHT (SULFUR, LECO, HIGH TEMP, 04239) 10ml  
Job ID NAP2000Z0J.M06-07227  
Job Desc: Diesel Fuel from B. Govt.

10 Numeric

155377 20453-045-1

ORGANIC LAYER

(TEMPLATE FOR DIESEL)

DEE.OELCOSHT	SULFUR, LECO HIGH TEMP, 04239	10 ml
OENPPM WATL	Nitrogen ppm-w in oils & water	2g
CC711N	TOTAL Acn #	26g

NAP2000Z0J.M06-07228

10 Numeric

155378 20453-046-1

Work By \_\_\_\_\_ Continued on Page \_\_\_\_\_

Recorded By \_\_\_\_\_ Date \_\_\_\_\_

Read and Understood By \_\_\_\_\_ Date \_\_\_\_\_



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